

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 October 2002 (24.10.2002)

PCT

(10) International Publication Number
WO 02/083699 A2

(51) International Patent Classification⁷: C07F 17/00

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(21) International Application Number: PCT/EP02/03697

(81) Designated States (national): JP, US.

(22) International Filing Date: 3 April 2002 (03.04.2002)

(84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(25) Filing Language: English

Declaration under Rule 4.17:

— of inventorship (Rule 4.17(iv)) for US only

(26) Publication Language: English

Published:

— without international search report and to be republished upon receipt of that report

(30) Priority Data:

01201327.2 10 April 2001 (10.04.2001) EP

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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WO 02/083699 A2

(54) Title: PROCESS FOR THE PRODUCTION OF MONOHALIDE OR DIHALIDE METALLOCENE COMPOUNDS

(57) Abstract: A process for preparing dihalide or monohalide metallocene compounds comprising contacting a compound of formula (II) $(Cp)(ZR^{1m})_n(A)_rML^y$ (II) wherein Cp is a cyclopentadienyl radical; $(ZR^{1m})_n$ is a divalent bridging group between Cp and A; A is a cyclopentadienyl radical or O, S, NR², PR² wherein R² is an hydrocarbon radical, M is zirconium, titanium or hafnium, L' is an hydrocarbon radical, r ranges from 0 to 2 and y is equal to 4; with an halogenating agent selected from the group consisting of: $T^1L_w^1$ wherein T¹ is a metal of groups 3-13 of the periodic table; L is halogen and w¹ is equal to the oxidation state of the metal T¹; $T^2L_w^2$ wherein T² is a nonmetal element of groups 13-16 of the periodic table (new IUPAC version); and w² is equal to the oxidation state of the element T²; $O=T^3L_w^3$ where T³ is a selected from the group consisting of C, P and S; O is an oxygen atom bonded to T³ trough a double bond; and w³ is equal to the oxidation state of the element T³ minus 2; $R^6C(O)L$, wherein R⁶ is an hydrocarbon radical; L₂ and HL.

PROCESS FOR THE PRODUCTION OF MONOHALIDE OR DIHALIDE METALLOCENE COMPOUNDS

The present invention relates to a process for the production of monohalide or dihalide metallocene compounds in high purity and in high yields.

Metallocene compounds are well known in the art as catalyst components for the polymerization of olefins. For instance, the European Patent Application EP 0 129 368 discloses catalysts comprising mono- and di-cyclopentadienyl coordination complexes with a transition metal in combination with an alumoxane.

In those metallocene compounds, the central metal is coordinated with one or more π -bonded ligands, usually cyclopentadienyl moieties, and with one or more sigma-bonded ligands. The latter are usually halogen, preferably chlorine. In the usual process for preparing dihalide metallocene compounds the lithium salts of the ligands are contacted with a tetrahalide of the metal. This process generates LiCl as a by-product that is difficult to separate because of the low solubility of the dihalide metallocene compounds in the usual solvents, and often the yield of the process is not satisfactory.

For instance, F. Wild et al. (*J. Organomet. Chem.*, 288:63-67, 1985) describe the synthesis of chiral ansa-zirconocene derivatives with ethylene-bridged ligands. In particular, it is reported the preparation of ethylene-bis(1-indenyl)zirconium dichloride by reaction of the dilithium salt of bis(1-indenyl)ethane with $ZrCl_4$, in a yield of about 35%. Better results have been obtained by I.M. Lee et al. (*Organometallics*, 11:2115-2122, 1992), who prepared ethylene-bis(1-indenyl)zirconium dichloride in a yield of 52%. Another example can be found in *Polyhedron* 1990, 9, 301 wherein it is reported the synthesis of bis(indenyl)zirconium dichloride starting from indene and zirconium tetrachloride with a final yield of 58%.

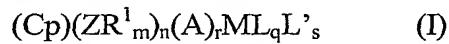
In *Izv. Akad. Nauk SSSR, Ser. Khim.* 1976, 2621 there is described a reaction of mercury chloride ($HgCl_2$) with bis(cylopentadienyl)zirconium dibenzyl. In this paper it is shown that, instead of the expected bis(cylopentadienyl)zirconium dichloride, the reaction product is the complex $(C_5H_5)_2ZrCl_2x3C_6H_5CH_2HgCl$.

In *Dokl. Akad. Nauk SSSR* (1976), 231(1), 114-15, G. A. Razuvayev investigates the mechanism of photo or thermo demethylation and dearylation by using bis(cylopentadienyl)zirconium dimethyl or dibenzyl and carbon tetrachloride or chloroform. The reaction is slow (about 100 h at 150°C for the thermodemethylation) and moreover the yields are rather low.

A process for obtaining bis(cyclopentadienyl)zirconium chloride methyl has been described by Wailes in Journal of Organometallic Chemistry 1972, 34, 155. According to this process, bis(cyclopentadienyl)zirconium chloride methyl is obtained by reacting the dimethyl derivative with $PbCl_2$. The yield of this process is not reported. The applicant by running a test according to the process described by Wailes (reported as comparative example 11) has found that the yield of this process is not satisfactory for an industrial process.

Therefore it is felt the need for a simpler and more convenient and practical method to produce the above metallocene derivatives in satisfactory yields.

This need is fulfilled according to the present invention that, according to a first object, relates to a process for preparing dihalide or monohalide metallocene compounds of formula (I):



wherein $(ZR^1m)_n$ is a divalent group bridging the Cp and A moieties; Z being C, Si, Ge, N or P, and the R^1 groups, equal to or different from each other, being hydrogen or linear or branched, saturated or unsaturated C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} alkylaryl or C_7-C_{20} arylalkyl groups, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements, or two R^1 can form an aliphatic or aromatic C_4-C_7 ring that can bear substituents;

Cp is an unsubstituted or substituted cyclopentadienyl group, optionally condensed to one or more unsubstituted or substituted, saturated, unsaturated or aromatic rings, containing from 4 to 6 carbon atoms, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

A is O, S, NR^2 or PR^2 , R^2 being hydrogen, a linear or branched, saturated or unsaturated C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} alkylaryl or C_7-C_{20} arylalkyl, or A has the same meaning of Cp;

M is zirconium, titanium or hafnium, preferably being zirconium or hafnium;

the L substituents, equal to or different from each other, preferably equal, are chlorine, bromine, iodine, preferably chlorine;

L' is selected from the group consisting of hydrogen, a linear or branched, saturated or unsaturated C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} alkylaryl or C_7-C_{20} arylalkyl group, optionally containing one or more Si or Ge atoms; preferably L' is methyl, ethyl, n-butyl, sec-butyl, phenyl, benzyl or $-CH_2Si(CH_3)_3$; more preferably L' is methyl;

m is 1 or 2 depending on the oxidation state of Z, more specifically it is 1 when Z is N or P, and

it is 2 when Z is C, Si or Ge;

n is 0, 1, 2, 3 or 4, preferably it is 0, 1 or 2; being 0 when r is 0 or 2;

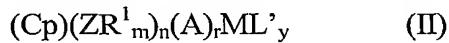
r is 0, 1 or 2, preferably being 0 or 1;

q is 1, 2, or 3;

s is 0 or 1;

s and q satisfying the following equation: q+s=3-r; preferably q is 1 or 2 and s is 0 or 1; more preferably q is 2 and s is 0;

said process comprising contacting a compound of formula (II):



wherein y is equal to s+q and Cp, Z, R¹, A, M, L', m, r, n, s and q have the same meaning as above,

with an halogenating agent selected from the group consisting of T¹L_w¹, T²L_w², O=T³L_w³, R⁶C(O)L, L₂ and HL, mercury dichloride (HgCl₂) being excluded, wherein:

T¹ is a metal of groups 3-13 of the periodic table (new IUPAC version) or of the lanthanides series; preferably T¹ is a metal of groups 7-11 of the periodic table (new IUPAC version);

T² is a nonmetal element of groups 13-16 of the periodic table (new IUPAC version) with the exclusion of carbon;

T³ is selected from the group consisting of C, P and S;

O is an oxygen atom bonded to T³ through a double bond;

R⁶ is selected from a linear or branched, saturated or unsaturated C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl or C₇-C₂₀ arylalkyl;

L has the same meaning as above;

H is hydrogen;

w¹ is equal to the oxidation state of the metal T¹;

w² is equal to the oxidation state of the element T²;

w³ is equal to the oxidation state of the element T³ minus 2.

The compound of formula (II) are well known in the art for example they can be easily prepared as described in WO 99/36427 or WO 00/75151.

An alternative embodiment for preparing dihalide or monohalide metallocene compounds of formula (I) starting directly from the ligand without isolating the compound of formula (II) comprises the following steps:

- a) reacting a ligand of formula (Y-Cp)(ZR¹_m)_n(A-Y)_r or when n is 0 a mixture of ligands Y-

Cp and $r(A-Y)$ with an amount EQ of a compound of formula L'_jB or $L'MgL''$ such that $EQ \geq 1+r$ molar equivalents with respect to Cp , preferably $1+r \leq EQ \geq 1+r+q$ molar equivalents; more preferably $EQ = 1+r+q$ molar equivalents, wherein Cp , A , Z , R^1 , m , r , q , and L' have the meaning reported above; L'' is selected from the group consisting of chlorine, bromine, iodine; n is an integer having values 1, 2, 3 or 4; the groups Y , the same or different from each other, are suitable leaving groups; Mg is magnesium; B is an alkaline or alkaline-earth metal; and j is 1 or 2, j being equal to 1 when B is an alkali metal, and j being equal to 2 when B is an alkaline-earth metal;

- b) reacting the product obtained from step a) with at least 1 molar equivalent with respect to Cp of a compound of formula ML''_4 , wherein M have the meaning reported above, L'' is selected from the group consisting of chlorine, bromine, iodine;
- c) if the amount EQ of a compound of formula L'_jB or $L'MgL''$ added in step a) is less than $1+r+q$, adding to the reaction mixture an amount of a compound of formula L'_jB or $L'MgL''$ equal to or higher than $1+r+q-EQ$ molar equivalents, preferably equal to $1+r+q-EQ$;
- d) optionally purifying the mixture and separating the meso and the rac forms; and
- e) reacting the mixture with an halogenating agent selected from the group consisting of: $T^1L_w^1$; $T^2L_w^2$; $O=T^3L_w^3$; $R^6C(O)L$; L_2 and HL wherein T^1 , T^2 , T^3 , L , w^1 , w^2 , w^3 and R^6 have been described above.

When n is different from 0 and r is 1 a preferred process for preparing the dihalide or monohalide of bridged metallocene compounds of formula (III)



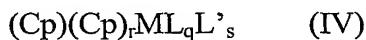
wherein M , Cp , A , Z , R^1 , m , q , s , L and L' have the meaning reported above and n is an integer having values 1, 2, 3 or 4; comprises the following steps:

- a) reacting a ligand of formula $(Y-Cp)(ZR^1_m)_n(A-Y)$ with at least $2+q$ molar equivalents with respect to Cp , of a compound of formula L'_jB or $L'MgL''$, wherein Cp , A , Z , R^1 , m , q , and L' have the meaning reported above; L'' is selected from the group consisting of chlorine, bromine, iodine; n is an integer having values 1, 2, 3 or 4; the groups Y , the same or different from each other, are suitable leaving groups; Mg is magnesium; B is an alkaline or alkaline-earth metal; and j is 1 or 2, j being equal to 1 when B is an alkali metal, and j being equal to 2 when B is an alkaline-earth metal; and
- b) reacting the product obtained from step a) with at least 1 molar equivalent of a compound

of formula ML''_4 , wherein M have the meaning reported above, L'' is selected from the group consisting of chlorine, bromine, iodine;

- c) optionally purifying the mixture and separating the racemic and the meso forms;
- d) reacting the mixture with an halogenating agent selected from the group consisting of: $T^1L_w^1$; $T^2L_w^2$; $O=T^3L_w^3$; $R^6C(O)L$; L_2 and HL wherein T^1 , T^2 , T^3 , L , w^1 , w^2 , w^3 and R^6 have been described above.

When A is equal to Cp and n is equal to 0 a preferred process for preparing metallocene compounds of formula (IV)



wherein M, Cp, M, L, L', r, q and s have been described above

comprises the following steps:

- a) reacting $1+r$ equivalent of a ligand of formula (Y-Cp) with at least $3+r$ molar equivalents of a compound of formula L_jB or $L''''MgL'$, wherein Cp, L'''' and L' have the meaning reported above; the groups Y, the same or different from each other, are suitable leaving groups; B is an alkaline or alkaline-earth metal; and j is 1 or 2, j being equal to 1 when B is an alkali metal, and j being equal to 2 when B is an alkaline-earth metal;
- b) reacting the product obtained from step a) with at least 1 molar equivalent of a compound of formula ML''_4 , wherein M have the meaning reported above, L'' is selected from the group consisting of chlorine, bromine, iodine;
- c) optionally purifying the mixture; and
- d) reacting the mixture with an halogenating agent selected from the group consisting of: $T^1L_w^1$; $T^2L_w^2$; $O=T^3L_w^3$; $R^6C(O)L$; L_2 and HL wherein T^1 , T^2 , T^3 , L , w^1 , w^2 , w^3 , R^6 have been described above.

According to a preferred embodiment of the present invention, all the reactions of the above processes are carried out in an aprotic solvent, either polar or apolar. Said aprotic solvent is preferably an aromatic or aliphatic hydrocarbon, optionally halogenated, or an ether, more preferably it is selected from the group consisting of benzene, toluene, pentane, hexane, heptane, cyclohexane, dichloromethane, diethylether, tetrahydrofuran or mixtures thereof.

The amount of the halogenating agent to be used depends from the type of compound. As a rule, for obtaining a monohalide metallocene compounds at least half equivalent with respect to the halogen atom has to be used, while for obtaining a dihalide derivative at least one equivalent with respect to the halogen atom has to be used. Excess of halogenating agent can

also be used.

The Y leaving group is preferably hydrogen.

The ML''_4 reactant, is preferably selected from the group consisting of $TiCl_4$, $ZrCl_4$, $HfCl_4$. It can be used even in the form of a stabilized derivative, such as an etherate complex of ML''_4 , easily available on the market.

The compounds L'_jB and $L''''MgL'$ are alkylating agents. Preferably L' is selected from the group consisting of methyl, ethyl, n-butyl, sec-butyl, phenyl, benzyl and $-CH_2Si(CH_3)_3$. More preferably L' is methyl.

In the compound L'_jB , B is an alkali or alkaline-earth metal, preferably Li or Mg; j can be 1 or 2, as already reported.

The compound $L''''MgL'$ is a Grignard reagent, wherein Mg is magnesium and L'''' and L' have the meanings reported above. L'''' is preferably bromine or iodine.

According to a preferred embodiment of the process of the invention, said alkylating agent is methyl lithium.

Preferably in the processes for preparing compounds of formula (I), (III) and (IV) in step (a), the ligands are previously dissolved in an aprotic polar solvent and to the resulting solution is added the alkylating agent L'_jB or $L''''MgL'$. This addition is preferably carried out at a temperature ranging from $-100^\circ C$ to $+80^\circ C$, more preferably from $-80^\circ C$ to $+10^\circ C$, over a period of 5 to 45 minutes, more preferably of 10 to 20 minutes. The alkylating agent is preferably added in the form of a solution in one of the above mentioned aprotic solvents, preferably dropwise.

The thus obtained reaction mixture is preferably allowed to react, under stirring, for a period ranging from 1 to 6 hours, more preferably from 2 to 3 hours, at a temperature comprised between $-10^\circ C$ and $+80^\circ C$, more preferably at room temperature.

Before the reaction with ML''_4 , in step (b), the mixture obtained from step (a) is preferably cooled to a temperature ranging from $-100^\circ C$ to $+80^\circ C$, more preferably from $-80^\circ C$ to $+70^\circ C$. Then ML''_4 is quickly added to the cooled slurry in the form of a solution in one of the above mentioned aprotic solvents, preferably pentane, hexane, heptane or toluene.

The reaction mixture is then allowed to react for a period ranging from 10 minutes to 36 hours, more preferably from 1 to 18 hours, at a temperature comprised between $-100^\circ C$ and $+80^\circ C$, more preferably between $-50^\circ C$ and $+50^\circ C$, even more preferably at room temperature.

In the halogenating step the temperature ranges from $-50^\circ C$ to $+150^\circ C$, preferably from $0^\circ C$ to $100^\circ C$, more preferably from $20^\circ C$ to $50^\circ C$. The halogenating agent is generally added

dropwise and then the reaction mixture is preferably allowed to react, under stirring, for a period ranging from 1 to 6 hours, more preferably from 2 to 3 hours, at a temperature comprised between -10°C and +80°C, more preferably at room temperature.

The thus obtained metallocene compounds of formulas (I), (III) and (IV) can be isolated according to the common procedures known in the state of the art.

Non limiting examples of halogenating agents of formula $T^1L_w^1$ are: $FeCl_3$, $CuCl_2$ and $ZnCl_2$.

Non limiting examples of halogenating agents of formula $T^2L_w^2$ are: BCl_3 , BBr_3 , $SiCl_4$ and PCl_5 .

Non limiting examples of halogenating agents of formula $O=T^3L_w^3$ are: $SOCl_2$ and $POCl_3$.

Non limiting examples of halogenating agents of formula $R^6C(O)L$ are: $CH_3C(O)Cl$, $C_6H_5CH_2C(O)Cl$, $C_6H_5C(O)Cl$ and $CH_3CH_2CH_2C(O)Cl$.

Non limiting examples of halogenating agents of formula L_2 are: Br_2 , Cl_2 and I_2 .

Non limiting examples of halogenating agents of formula HL are HCl , HBr and HI .

In the optional steps (c) and (d) the purification of the reaction mixture is preferably carried out by simply filtering the solution in order to remove the salts. Also other systems of purification can be used, for example a suitable solvent in order to precipitate the undesired by products can be added with subsequently filtration. In these steps it is also possible to separate (when present) the racemic and the meso form by using methods known in the art. For example, by using suitable solvents it is possible to precipitate one form with subsequently filtration. All the operations are carried out in inert atmosphere.

In the metallocenes of formula (I) and (III), the divalent bridge $(ZR^1_m)_n$ is preferably selected from the group consisting of CR^1_2 , $(CR^1_2)_2$, $(CR^1_2)_3$, SiR^1_2 , GeR^1_2 , NR^1 and PR^1 , R^1 having the meaning reported above. More preferably, said divalent bridge is $Si(CH_3)_2$, $SiPh_2$, CH_2 , $(CH_2)_2$, $(CH_2)_3$ or $C(CH_3)_2$.

The variable m is 1 or 2; the variable n ranges from 0 to 4 preferably is 1 or 2, when $n > 1$, the atoms Z can be the same or different from each other, such as in divalent bridges $-CH_2-O-$, $-CH_2-S-$ and $-CH_2-Si(CH_3)_2-$. When $n = 0$ and $r = 1$, A can have only the meaning of Cp .

In the metallocenes of formula (I), (III) and (IV) the ligand Cp , which is π -bonded to said metal M , is preferably selected from the group consisting of cyclopentadienyl, mono-, di-, tri- and tetra-methyl cyclopentadienyl; 4-tertbutyl-cyclopentadienyl; 4-adamantyl-cyclopentadienyl; indenyl; mono-, di-, tri- and tetra-methyl indenyl; 4,5,6,7-tetrahydroindenyl; fluorenyl; 5,10-dihydroindeno[1,2-b]indol-10-yl; N-methyl- or N-phenyl-5,10-dihydroindeno [1,2-b]indol-10-yl;

5,6-dihydroindeno[2,1-b]indol-6-yl; N-methyl- or N-phenyl-5,6-dihydroindeno[2,1-b]indol-6-yl; azapentalene-4-yl; thiapentalene-4-yl; azapentalene-6-yl; thiapentalene-6-yl; mono-, di- and tri-methyl-azapentalene-4-yl and 2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene.

The group A has preferably the same meaning of Cp, or it is N- methyl, N-ethyl, N-isopropyl, N- butyl, N-phenyl, N-benzyl, N-cyclohexyl and N-cyclododecyl.

Non limiting examples of metallocene compounds of formula (I) , (III) and (IV) are the racemic and the meso form (when present) of the following compounds:

bis(cyclopentadienyl)zirconium dichloride;

bis(indenyl)zirconium dichloride;

bis(tetrahydroindenyl)zirconium dichloride;

bis(fluorenyl)zirconium dichloride;

dimethylsilanediylbis(indenyl)zirconium dichloride,

dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride,

dimethylsilanediylbis(4-naphthylindenyl)zirconium dichloride,

dimethylsilanediylbis(2-methylindenyl)zirconium dichloride,

dimethylsilanediylbis(2-methyl-(4-t-butyl-phenyl) indenyl)zirconium dichloride,

dimethylsilanediylbis(2-methyl-4-isopropylindenyl)zirconium dichloride,

dimethylsilanediylbis(2,4-dimethylindenyl)zirconium dichloride,

dimethylsilanediylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride,

dimethylsilanediylbis(2,4,7-trimethylindenyl)zirconium dichloride,

dimethylsilanediylbis(2,4,6-trimethylindenyl)zirconium dichloride,

dimethylsilanediylbis(2,5,6-trimethylindenyl)zirconium dichloride,

methyl(phenyl)silanediylbis(2-methyl-4,6-diisopropylindenyl)-

zirconium dichloride,

methyl(phenyl)silanediylbis(2-methyl-4-isopropylindenyl)-

zirconium dichloride,

1,3-propylenebis(indenyl)zirconium dichloride,

1,3-propylenebis(4,7-dimethylindenyl)zirconium dichloride,

1,3-propylenebis(2-methyl-4-phenylindenyl)zirconium dichloride,

1,3-propylenebis(2-methyl-4,6-diisopropylindenyl)zirconium dichloride,

1,3-propylenebis (2-methyl-4,5-benzoindenyl)zirconium dichloride,

1,2-ethylenebis(indenyl)zirconium dichloride,

1,2-ethylenebis(4,7-dimethylindenyl)zirconium dichloride,
1,2-ethylenebis(2-methyl-4-phenylindenyl)zirconium dichloride,
1,4-butanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride,
1,2- ethylenebis(2-methyl-4,6-diisopropylindenyl)zirconium dichloride,
1,4-butanediylbis(2-methyl-4-isopropylindenyl)zirconium dichloride,
1,4-butanediylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride,
1,2- ethylenebis (2-methyl-4,5-benzoindenyl)zirconium dichloride,
[4-(η^5 -cyclopentadienyl)-4,6,6-trimethyl(η^5 -4,5-tetrahydro-pentalene)]dichloridezirconium,
[4-(η^5 -3'-trimethylsilylcyclopentadienyl)-4,6,6-trimethyl(η^5 -4,5-tetrahydropentalene)]dichloridezirconium,
(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethane-dichloridetitanium,
(methylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilyl-dichloridetitanium,
(methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyl-dichloridetitanium,
(tertbutylamido)-(2,4-dimethyl-2,4-pentadien-1-yl)dimethylsilyl-dichloridetitanium,
bis(1,3-dimethylcyclopentadienyl)zirconium dichloride,
methylene(3-methyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dithiophene)zirconium dichloride;
methylene(3-isopropyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dithiophene)zirconium dichloride;
methylene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dithiophene)zirconium dichloride;
methylene(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'] dithiophene)zirconium dichloride;
methylene-1-(indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)zirconium dichloride;
methylene-1-(indenyl)-7-(2,5-ditrimethylsilylcyclopentadienyl-[1,2-b:4,3-b']dithiophene)zirconium dichloride;

methylene-1-(3-isopropyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)zirconium dichloride;
methylene-1-(2-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)zirconium dichloride;
methylene-1-(tetrahydroindenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)zirconium dichloride;
methylene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dioxazol)zirconium dichloride;
methylene(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dioxazol)zirconium dichloride;
methylene-1-(indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dioxazol)zirconium dichloride;
isopropylidene(3-methyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)zirconium dichloride;
isopropylidene(2,4-dimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)zirconium dichloride;
isopropylidene(2,4-diethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)zirconium dichloride;
isopropylidene(2,3,5-trimethyl-cyclopentadienyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)zirconium dichloride;
isopropylidene-1-(indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)zirconium dichloride;
isopropylidene-1-(2-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)zirconium dichloride;
dimethylsilandiyl-1-(2-methyl-indenyl)-7-(2,5-dimethylcyclopentadienyl-[1,2-b:4,3-b'])dithiophene)hafnium dichloride;
dimethylsilanediyl(3-tert-butyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,
dimethylsilanediyl(3-isopropyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,
dimethylsilanediyl(3-methyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,
dimethylsilanediyl(3-ethyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,
1-2-ethane(3-tert-butyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,
1-2-ethane (3-isopropyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,

1-2-ethane (3-methyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,
1-2-ethane (3-ethyl-cyclopentadienyl)(9-fluorenyl)zirconium dichloride,
dimethylsilandiylbis-6-(3-methylcyclopentadienyl-[1,2-b]-thiophene) zirconium dichloride;
dimethylsilandiylbis-6-(4-methylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(4-isopropylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(4-ter-butylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(3-isopropylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(2,5-dimethyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-[2,5-dimethyl-3-(2-methylphenyl)cyclopentadienyl-[1,2-b]-thiophene]zirconium dichloride;
dimethylsilandiylbis-6-[2,5-dimethyl-3-(2,4,6-trimethylphenyl)cyclopentadienyl-[1,2-b]-thiophene]zirconium dichloride;
dimethylsilandiylbis-6-[2,5-dimethyl-3-mesitylenecyclopentadienyl-[1,2-b]-thiophene]zirconium dichloride;
dimethylsilandiylbis-6-(2,4,5-trimethyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(2,5-diethyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(2,5-diisopropyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(2,5-diter-butyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(2,5-ditrimethylsilyl-3-phenylcyclopentadienyl-[1,2-b]-thiophene)zirconium dichloride;
dimethylsilandiylbis-6-(3-methylcyclopentadienyl-[1,2-b]-silole)zirconium dichloride;
dimethylsilandiylbis-6-(3-isopropylcyclopentadienyl-[1,2-b]-silole)zirconium dichloride;
dimethylsilandiylbis-6-(3-phenylcyclopentadienyl-[1,2-b]-silole)zirconium dichloride;
dimethylsilandiylbis-6-(2,5-dimethyl-3-phenylcyclopentadienyl-[1,2-b]-silole)zirconium dichloride;
dimethylsilandiylbis-6-[2,5-dimethyl-3-(2-methylphenyl)cyclopentadienyl-[1,2-b]-

silole]zirconium dichloride;
dimethylsilandiylbis-6-[2,5-dimethyl-3-(2,4,6-trimethylphenyl)cyclopentadienyl-[1,2-b]-silole]zirconium dichloride;
dimethylsilandiylbis-6-[2,5-dimethyl-3-mesitylenecyclopentadienyl-[1,2-b]-silole]zirconium dichloride;
dimethylsilandiylbis-6-(2,4,5-trimethyl-3-phenylcyclopentadienyl-[1,2-b]-silole)zirconium dichloride;
[dimethylsilyl(tert-butylamido)][(N-methyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;
[dimethylsilyl(tert-butylamido)][(6-methyl-N-methyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;
[dimethylsilyl(tert-butylamido)][(6-methoxy-N-methyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;
[dimethylsilyl(tert-butylamido)][(N-ethyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;
[dimethylsilyl(tert-butylamido)][(N-phenyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;
[dimethylsilyl(tert-butylamido)][(6-methyl-N-phenyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;
[dimethylsilyl(tert-butylamido)][(6-methoxy-N-phenyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;
[dimethylsilyl(tert-butylamido)][(N-methyl-3,4-dimethyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;
[dimethylsilyl(tert-butylamido)][(N-ethyl-3,4-dimethyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;
[dimethylsilyl(tert-butylamido)][(N-phenyl-3,4-dimethyl-1,2-dihydrocyclopenta[2,1-b]indol-2-yl)]titanium dichloride;
as well as the correspondent titanium and hafnium compounds and the dibromide and diiodide compounds.
The process according to the present inventions shows several advantages with respect to the processes generally known in the state of the art. The overall yields starting from the ligands

are generally higher than those reported in the art. Moreover, it is easier to purify the desired product, due to the better solubility of the formed intermediate alkylated metallocene with respect to the dihalide or monohalide product. Further, because of the higher solubility of said intermediate metallocene it is also easy to separate the racemic and the meso form at this step and thus to obtain the substantially pure racemic or meso form as the final product.

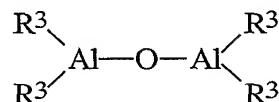
The metallocene compounds obtained with the process according to the present invention, in combination with a suitable activator such as an alumoxane, can be used as a catalyst for the polymerization of olefins. Particularly, they can be used for the homo or co-polymerization of alpha-olefins of formula $\text{CH}_2=\text{CHR}$ wherein R is hydrogen or a $\text{C}_1\text{-C}_{20}$ alkyl, such as propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene and 1-octene.

An interesting use is for the production of isotactic, syndiotactic or atactic polypropylene.

Another interesting use is for the copolymerization of ethylene with alpha-olefins, such as propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene and 1-octene, with cycloolefins, such as cyclopentene, cyclohexene, norbornene and 4,6-dimethyl-1-heptene, or with polyenes, such as 1,4-hexadiene, isoprene, 1,3-butadiene, 1,5-hexadiene and 1,6-heptadiene.

Further, they can be advantageously used in olefin oligomerization or hydrogenation reactions.

The above metallocenes form suitable polymerization catalytic systems in association with alumoxanes of formula:



wherein the substituents R^3 can be a linear or branched, saturated or unsaturated, $\text{C}_1\text{-C}_{20}$ alkyl, alkenyl or alkylaryl radical;

or in association with the product obtained by contacting an organometallic aluminum compound of formula $\text{AlR}^5_{3-z}\text{H}_z$, wherein R^5 can be $\text{C}_1\text{-C}_{10}$ alkyl, alkenyl or alkylaryl radicals, optionally containing one or more Si or Ge atoms, with water.

Particularly suitable alumoxanes, acting as cocatalysts with the above metallocenes, are methylalumoxane (MAO), tris(2-methyl-propyl)alumoxane (TIBAO) and 2,4,4-trimethyl-pentylalumoxane (TIOAO).

Non-limiting examples of organometallic aluminum compounds that, upon contacting with water, produce suitable cocatalysts are trimethylaluminum (TMA), tris(2,4,4-trimethyl-pentyl)aluminum (TIOA), tris(2-methyl-propyl)aluminum (TIBA), tris(2,3,3-trimethyl-butyl)aluminum, tris(2,3-dimethyl-hexyl)aluminum, tris(2,3-dimethyl-butyl)aluminum,

tris(2,3-dimethyl-pentyl)aluminum, tris(2,3-dimethyl-heptyl)aluminum, tris(2-methyl-3-ethyl-pentyl)aluminum and tris(2-ethyl-3,3-dimethyl-butyl).

The above catalysts can suitably be used on inert supports, such as silica, alumina, styrene/divinylbenzene copolymers, polyethylene or polypropylene, particularly for use in the gas phase polymerizations.

The olefin polymerization processes can be carried out in liquid phase, optionally in the presence of an inert hydrocarbon solvent, either aromatic (e.g. toluene) or aliphatic (e.g. propane, hexane, heptane, isobutane, cyclohexane and 2,2,4-trimethylpentane). The polymerization temperature generally ranges from about 0°C to about 250°C, and preferably from 20 to 150°C.

The following examples are given for illustrative and not limitative purposes.

GENERAL PROCEDURES AND CHARACTERIZATIONS

All operations were performed under nitrogen by using conventional Schlenk-line techniques. Solvents were purified by degassing with N₂ and passing over activated (8 hours, N₂ purge, 300 °C) Al₂O₃, and stored under nitrogen. MeLi (Acros), TiCl₄ (Aldrich), ZrCl₄ (Aldrich), HfCl₄ (Roc-Ric, 99.99% Hf), FeCl₃ (Aldrich), BCl₃ (Aldrich), CuCl (Carlo Erba, RPE-ACS, 95%) and SiCl₄ (Aldrich) were used as received. Technical indene (Aldrich) was purified by passing over activated Al₂O₃; All compounds were analyzed on an AC 200 Bruker spectrometer, by ¹H NMR (200.13 MHz, CD₂Cl₂, referenced against the middle peak of residual CHDCl₂ at 5.35 ppm, or C₆D₆, referenced against the peak of residual C₆D₅H at 7.15 ppm) and ¹³C NMR (50.323 MHz, Broad Band Decoupling, C₆D₆, referenced to the central line of C₆D₆ at 128.00 ppm). All NMR solvents were dried over P₄O₁₀ or CaH₂ and distilled before use. GC-MS analyses were carried out on a HP 5890 - series 2 gas-chromatograph and a HP 5970 mass spectrometer.

Comparative example 1 synthesis of Ind₂ZrCl₂

40 mL of a 1.5 M solution of BuLi in Et₂O (60 mmol) were added dropwise to 7.0 mL of indene (60.0 mmol) in 20 mL of THF, cooled to -78 °C. At the end of the addition, the solution was allowed to warm to room temperature and stirred for 1 hour, to give an orange solution. 7 g of ZrCl₄ (30.0 mmol) were dissolved in 30 mL of THF at -78 °C in a 100 mL flask equipped with reflux condenser (exothermic reaction). The mixture was allowed to reach room temperature with stirring, then refluxed for 30 min, to give a clear, brown solution. To this solution was added the THF solution of indenyllithium at room temperature with stirring, then the resulting suspension was stirred for two hours. The color turned yellow. The solvents

were removed under reduced pressure, the residue slurried in Et₂O and transferred into an extractor, washed with Et₂O until colorless, then extracted with CH₂Cl₂, the extract dried and washed again with Et₂O and then pentane, finally dried to give 4.35 g of yellow, analytically pure Ind₂ZrCl₂. Isolated yield 36.9 %.

Comparative example 2 synthesis of Ind₂ZrCl₂

9.9 mL of a 1.6 M solution of MeLi in Et₂O (15.8 mmol) were added dropwise to 1.97 g of technical indene (93.3 % by GC, 15.8 mmol) in 30 mL of Et₂O, at the end of the addition the mixture was stirred for 40 min at room temp., then it was added at once to 1.84 g of ZrCl₄ (7.9 mmol) slurried in 30 mL of pentane, then the resulting suspension was stirred for two hours. The color turned yellow. The product in pentane/Et₂O was transferred into an extractor, filtrated, the filtrate was discarded, the residue dried and extracted at reflux with 80 mL of CH₂Cl₂ for 5 hours. The extract was dried to give 2.08 g of lemon yellow Ind₂ZrCl₂, containing 4 mol% of Ind₂ZrClMe (¹H NMR). Isolated yield 67 %.

Example 3 synthesis of Ind₂ZrCl₂

Synthesis of Ind₂ZrMe₂.

15.8 ml of a solution of MeLi 1.6 M in Et₂O (25.3 mmol) were added at room temperature to a solution of 1.5 g (12.6 mmoles) of indene (Aldrich, 97.9 % by G.C.) in 30 ml of Et₂O in about 5 minutes (exothermic reaction). The mixture was stirred for 30 min, to give an orange solution. 1.47 g of ZrCl₄ (6.33 mmol) were slurried in 30 ml pentane. The ZrCl₄ slurry in pentane was quickly added to the Li salt solution in Et₂O (exothermic reaction). The reaction mixture was stirred for 30 min, and the yellow-brown suspension was treated as described above, to give 1.92 g (86.5 % yield) of a light yellow solid, which was characterized by ¹H NMR as spectroscopically pure Ind₂ZrMe₂.

Anal. Calcd for C₂₀H₂₀Zr: C, 68.32; H, 5.73; Zr, 25.94. Found: C, 67.3; H, 5.75; Cl, <0.05.

¹H-NMR (C₆D₆, δ, ppm): -0.50 (s, Ti-CH₃, 6H), 5.37 (t, Cp-H(2), 2H, J = 3.24 Hz), 5.78 (d, Cp-H(1,3), 4H, J = 3.24 Hz), 6.90-6.95 (m, Ar, 4H), 7.16-7.22 (m, Ar, 4H).

Synthesis of Ind₂ZrCl₂.

0.33 g of Ind₂ZrMe₂ (0.94 mmol) were charged in a 10 mL Schlenk tube, and dissolved in 4 mL of CD₂Cl₂. 0.485 g of CuCl (Carlo Erba, 95 %, 4.65 mmol) were added, and the mixture stirred at room temperature for 6 hours, when ¹H NMR showed the reaction to be complete. 20 mL of CH₂Cl₂ were added and the mixture was filtered over a G4 frit. The yellow-green solution was brought to dryness to give 0.34 g of yellow-green powder (yield 93 %) whose ¹H

NMR is identical to that of a true sample of $\text{Ind}_2\text{ZrCl}_2$.

^1H NMR (CD_2Cl_2 , δ , ppm): 6.23 (d, H(1-3), 4H, J = 3.32 Hz), 6.55 (t, H(2), 2H, J = 3.32 Hz), 7.28-7.37 (m, Ar, 4H), 7.60-7.69 (m, Ar, 4H).

Example 4 synthesis of $\text{Ind}_2\text{ZrCl}_2$

2.5 g of indene (92 %wt by GC, 19.8 mmol) were dissolved in 30 mL of Et_2O in a 250 mL Schlenk tube. 24.8 mL of MeLi 1.6 M in Et_2O (39.7 mmol) were added with stirring at room temperature (exothermic reaction). After stirring for 40 min, a yellow-orange solution was obtained, to which was added a suspension of 2.3 g of ZrCl_4 (9.9 mmol) in 40 mL of pentane (exothermic reaction, the mixture turns dark brown). The mixture was stirred at room temperature for two hours, then concentrated under reduced pressure to give a black powder, which was slurried in 50 mL of CH_2Cl_2 , cooled to 0°C, and added of 9.9 mL of BCl_3 1M in heptane (9.9 mmol). During the addition, the mixture turns from dark grey to dark green. This was allowed to warm to room temperature and stirred for 30 min at room temperature (complete conversion to the dichloride observed by ^1H NMR at this time), then filtered and extracted with the same CH_2Cl_2 for 8 hours on a continuous extractor (the product precipitates in part as a yellow solid during extraction), the extract concentrated under reduced pressure to give a yellow powder, 3.74 g (96 % yield based on Zr) of spectroscopically pure $\text{Ind}_2\text{ZrCl}_2$.

Example 5 synthesis of $\text{Ind}_2\text{ZrCl}_2$

0.25 g of $\text{Ind}_2\text{ZrMe}_2$ (0.71 mmol) were dissolved in 10 mL of CH_2Cl_2 in a 25 mL Schlenk tube, and 0.71 mL of BCl_3 1M in heptane (0.71 mmol) were added, a yellow precipitate start forming, and the slurry was stirred at room temperature for 1 hour, when ^1H NMR showed the conversion to $\text{Ind}_2\text{ZrCl}_2$ to be quantitative. The yellow suspension was brought to dryness to give 0.27 g of yellow, powdery, analytically pure $\text{Ind}_2\text{ZrCl}_2$ (yield 97 %). Its ^1H NMR is identical to that of a true sample of $\text{Ind}_2\text{ZrCl}_2$.

Example 6 synthesis of $\text{Ind}_2\text{ZrCl}_2$

0.172 g of $\text{Ind}_2\text{ZrMe}_2$ (0.49 mmol) were slurried in 5 mL of hexanes in a 10 mL Schlenk tube, and 0.49 mL of BCl_3 1M in heptane (0.49 mmol) were added at room temperature, and the mixture stirred for 2 hours, to give a 45:55 mixture of $\text{Ind}_2\text{ZrCl}_2$ and $\text{Ind}_2\text{ZrClMe}$ (^1H NMR), additional 0.3 mL of BCl_3 1M in heptane (0.3 mmol) and stirred for additional 2 hours. At this point the reaction is complete and the product is analytically pure by ^1H NMR.

Example 7 synthesis of $\text{Ind}_2\text{ZrCl}_2$

300 mg of $\text{Ind}_2\text{ZrMe}_2$ (20790/21, 0.85 mmol) were dissolved in 20 mL of Et_2O in a 50 mL

Schlenk tube. 0.95 mL of a 2M solution of HCl in Et₂O (Aldrich, 1.71 mmol) were added at room temperature. Gas evolution (CH₄) is observed, together with instantaneous formation of a yellow precipitate. Removing the solvent under reduced pressure gives 320 mg of pure Ind₂ZrCl₂, yield 96 %.

Example 8 synthesis of Ind₂ZrMeCl

380 mg of Ind₂ZrMe₂ (20790/21, 1.08 mmol) were dissolved in 5 mL of CH₂Cl₂ in a 10 mL Schlenk tube. 175 mg of anhydrous FeCl₃ (Aldrich, 99.9%, 1.08 mmol) were added at room temperature (immediate darkening to black), and then the mixture is heated at 40 °C for 6 hours. After 3 hours ¹H NMR shows the presence of a 98:2 mixture of Ind₂ZrClMe and residual Ind₂ZrMe₂ (yield of Ind₂ZrMeCl 98%).

Example 9 synthesis of Ind₂ZrI₂

164 mg of Ind₂ZrMe₂ (0.46 mmol) were dissolved in 2 mL of CD₂Cl₂ in a 10 mL Schlenk tube. 120 mg of I₂ crystals (0.47 mmol) were added at room temperature. The solution was warmed to 40 °C. After 5 min stirring the I₂ is fully solubilized, to give a bright orange solution that was stirred for 6 hours at 40 °C. ¹H-NMR analysis shows the presence of residual Ind₂ZrMe₂, and the two reaction products Ind₂ZrIMe and Ind₂ZrI₂, in the ratio 6:67:27.

Additional 60 mg of I₂ were added, and the solution stirred at room temperature for 72 hours. ¹H-NMR analysis shows conversion to the target Ind₂ZrI₂.

Ind₂ZrIMe: ¹H-NMR (CD₂Cl₂, δ, ppm): -1.47 (s, 3 H, Zr-CH₃), 6.09 (t, 2H, Cp-H2, J = 3.52 Hz), 6.39 (m, 2H, Cp-H(1,3)), 6.54 (m, 2H, Cp-H(3,1)), 7.23-7.28 (m, 2H, Ar), 7.64-7.69 (m, 2H, Ar).

Ind₂ZrI₂: ¹H-NMR (CD₂Cl₂, δ, ppm): 2.19 (CH₃I, cfr. CH₃I in CDCl₃ = 2.16 ppm); 6.42 (d, Cp-H(1,3), 4H, J = 3.33), 6.64 (t, Cp-H(2), 2H, J = 3.33), 7.30-7.40 (m, Ar, 4H), 7.66-7.75 (m, Ar, 4H).

Example 10 synthesis of Ind₂TiClMe

Synthesis Ind₂TiMe₂

31.0 mL of MeLi 1.6 M in Et₂O (49.6 mmol) were added with stirring at room temperature to a solution of 3 g of indene (94 % by G.C., 24.3 mmol) in 30 mL of diethyl ether over a period of about 10 minutes (exothermic reaction). The Schlenk tube was kept in a water bath to remove the heat of reaction. The reaction mixture was stirred for 30 minutes. After this time the solution turned from light yellow to orange. 1.34 mL of TiCl₄ (99 %, 12.2 mmol) were

dissolved in 30 mL of pentane, and this solution was quickly added to the Li salt solution (exothermic reaction). The reaction mixture was stirred for two hours at room temperature with final formation of a dark brown suspension. The solvents were then removed under reduced pressure. The brown solid obtained was extracted in a Soxhlet apparatus with 80 mL of pentane. The filtrate was evaporated to dryness under reduced pressure to give 2.62 g of a yellow-brown powder (70 % metal-based yield).

Anal. Calcd for $C_{20}H_{20}Ti$: C, 77.93; H, 6.54; Ti, 15.53. Found: C, 74.7; H, 6.35; Ti, 14.6; Cl, <0.05.

1H -NMR (C_6D_6 , δ , ppm): -0.50 (s, Ti-CH₃, 6H), 5.37 (t, Cp-H(2), 2H, J = 3.24 Hz), 5.78 (d, Cp-H(1,3), 4H, J = 3.24 Hz), 6.90-6.95 (m, Ar, 4H), 7.16-7.22 (m, Ar, 4H)

Synthesis Ind₂TiClMe

0.43 g of Ind₂TiMe₂ (20790/77, 1.4 mmol) were dissolved in 15 mL of toluene in a 50 mL Schlenk. 0.32 mL of SiCl₄ (99%, 2.79 mmol) were added at room temperature and the solution warmed up to 50 °C and stirred for 3 hours. 1H NMR reveals the formation of a 70:30 mixture of Ind₂TiClMe and Ind₂TiMe₂. To bring the reaction to completion, another 2 equivalents of SiCl₄ (0.32 mL) were added, and the red-orange solution stirred for 3 additional hours at 50 °C, then dried, to give a quantitative yield of Ind₂TiClMe as a brick red powder.

1H -NMR (C_6D_6 , δ , ppm): -0.08 (s, Ti-CH₃, 3H), 5.52 (t, Cp-H(2), 2H, J = 3.33 Hz), 5.80 (ddd, Cp-H(1 or 3), 2H, J = 0.88, 1.96, 3.33 Hz), 5.86 (ddd, Cp-H(3 or 1), 2H, J = 0.88, 1.96, 3.33 Hz), 6.85-7.31 (m, Ar, 8H).

Comparative example 11 synthesis of Ind₂ZrClMe

A slurry of 2.53 g of PbCl₂ (Aldrich, MW = 278.106, 9.10 mmol) in 15 mL of toluene was added to a solution of Ind₂ZrMe₂ (1.25 g, MW = 351.594, 3.56 mmol) in 35 mL of toluene, in a 100 mL Schlenk flask. The dark orange suspension obtained was stirred 38 hours at room temperature and 10 hours at 40-45 °C, during which time formation of a black powder was observed. The suspension was then filtered on a G4 frit and the filtrate was evaporated to dryness under reduced pressure to give 1.1 g of a dark yellow powder, which was characterized by 1H NMR as a mixture of Ind₂ZrMeCl and Ind₂ZrCl₂ in the ratio 90/10.

0.63 g of this mixture were treated with 30 mL of toluene and 1.2 g of PbCl₂ (4.31 mmol). The suspension obtained was stirred for 30 hours at room temperature and 12 hours at 40°C.

1H NMR analysis showed decomposition of the product to indene. The yield of the reaction

to give $\text{Ind}_2\text{ZrClMe}$ is 74%

Comparative example 12

0.67 g of CeCl_3 (Aldrich, MW = 246.48, 2.72 mmol) were added to a suspension of $\text{Ind}_2\text{ZrMe}_2$ (experiment 20826/5, 0.91 g, MW = 351.594, 2.59 mmol) in 30 mL of toluene, in a 100 mL Schlenk flask. The light brown suspension obtained was stirred 24 hours at room temperature, but no reaction was observed by ^1H NMR analysis. It was then treated with additional 0.64 g of CeCl_3 (2.6 mmol) and stirred 3 hours at room temperature and 4 hours at 40°C. No reaction was observed by ^1H NMR.

Example 13 synthesis of $\text{Ind}_2\text{ZrCl}_2$

A solution of SCl_2 (Riedel de Haen, 0.16 g, MW = 102.966, 1.55 mmol) in 10 mL of CH_2Cl_2 was added to a brown suspension of $\text{Ind}_2\text{ZrMe}_2$ (experiment 20826/7-9, 0.55 g, MW = 351.594, 1.56 mmol) in 10 mL of CH_2Cl_2 . During the addition exothermicity was observed and the reaction mixture turned clearer. After 3 hours stirring at room temperature the reaction mixture turned reddish and ^1H NMR analysis showed a mixture of $\text{Ind}_2\text{ZrCl}_2$ and $\text{Ind}_2\text{ZrMeCl}$ in the ratio 61/39. Additional 0.055 g of SCl_2 (0.53 mmol) were added to the reaction mixture. After 1 hour stirring the brown suspension obtained was evaporated to dryness under reduced pressure to give 0.61 g (100 % metal-based yield) of a clear brown powder, which ^1H NMR analysis showed to be $\text{Ind}_2\text{ZrCl}_2$ with some impurities.

Example 14 synthesis of Ind_2ZrI_2

Crystals of I_2 (0.70 g, MW = 253.809, 2.76 mmol) were added to a suspension of $\text{Ind}_2\text{ZrMe}_2$ (experiment 20826/7-9, 0.48 g, MW = 351.594, 1.36 mmol) in 20 mL of CH_2Cl_2 . The orange suspension turned to dark purple in few minutes. After 30 minutes stirring at room temperature, the suspension was evaporated to dryness under reduced pressure to give 0.83 g (100 % yield) of an orange powder, which was characterized by ^1H NMR as pure Ind_2ZrI_2 .

$^1\text{H-NMR}$ (CD_2Cl_2 , δ , ppm): 6.42 (d, 4H, Cp- $H(1,3)$, J = 3.33 Hz); 6.64 (t, 2H, Cp- $H(2)$, J = 3.33 Hz); 7.30-7.40 (m, 4H, Ar); 7.66-7.75 (m, 4H, Ar).

Example 15 synthesis of $\text{Ind}_2\text{ZrBr}_2$

A solution of 0.52 g of Br_2 (Fluka, 3.69 mmol) in 7 ml of CH_2Cl_2 was added to a solution of 0.65 g of $\text{Ind}_2\text{ZrMe}_2$ (1.85 mmol) in 20 ml of CH_2Cl_2 . The reaction was exothermic. The brown suspension obtained was stirred at room temperature for 18 hours and then evaporated to dryness under reduced pressure to give a reddish powder. This powder showed the presence of some impurity, so it was treated with ether and filtered. The residue was still not clean

enough, so it was treated with toluene and filtered. The filtrate was evaporated to dryness under reduced pressure to give pure $\text{Ind}_2\text{ZrBr}_2$ which was characterized by ^1H NMR.

^1H NMR (CD_2Cl_2 , δ , ppm): 6.28 (d, 4H, Cp-H(1,3), J = 3.42 Hz); 6.57 (t, 2H, Cp-H(2), J = 3.42 Hz); 7.30-7.38 (m, 4H, Ar); 7.63-7.70 (m, 4H, Ar).

Example 16 synthesis of $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(t\text{-BuN})\text{TiClMe}$

0.69 mL of SiCl_4 (5.98 mmoles) previously diluted in 2 mL of CH_2Cl_2 were added dropwise at room temperature to a solution of 0.98g of $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(t\text{-BuN})\text{TiMe}_2$ (obtained according to WO 00/75151) in 5 mL of CH_2Cl_2 . After 6h, the monochloro complex was obtained in nearly 100% yield.

Example 17 synthesis of (N-ethyl-5,6-dihydroindeno[2,1-b]indol-6-yl)(t-BuN)TiCl₂

0.71g of CuCl (6.85 mmoles) were added at room temperature to a solution of 0.6g (1.37 mmoles) of dimethylsilyl(*tert*-butylamino)(N-ethyl-5,6-dihydroindeno[2,1-b]indol-6-yl)dimethyl titanium (obtained according to WO 01/53360) in 5 mL of CH_2Cl_2 . The mixture of reaction was monitored by ^1H -NMR after 1 h, 4 h and one night of stirring. The suspension was filtered and the filtrate was dried in vacuo obtaining a red-brown sticky solid (yield 100%). ^1H -NMR shows the formation of dimethylsilyl(*tert*-butylamino)(N-ethyl-5,6-dihydroindeno[2,1-b]indol-6-yl)dichloro titanium.

Example 18 synthesis of (N-ethyl-5,6-dihydroindeno[2,1-b]indol-6-yl)(t-BuN)TiCl₂

0.7 mL (0.7 mmoles) of BCl_3 1.0 M in heptane were added at 0 °C to a solution of 0.306 g (0.7 mmoles) of dimethylsilyl(*tert*-butylamino)(N-ethyl-5,6-dihydroindeno[2,1-b]indol-6-yl)dimethyl titanium (obtained according to WO 01/53360) in 8 mL of Et_2O , after 2 hours of stirring at room temperature the ^1H -NMR analysis shows the formation of the dichloro complex. The solvent was dried in vacuo and the crude was washed with 7 mL of toluene, the residue was dried under reduced pressure, obtaining a red brown solid, which resulted almost pure desired product by ^1H -NMR (yield 100%).

^1H -NMR (C_6D_6 , δ , ppm): 0.61 (s, 3H, Si-CH₃); 0.75 (s, 3H, Si-CH₃); 1.15 (t, 3H, CH₃, J = 7.24 Hz); 1.28 (s, 9H, *t*-Bu); 3.81 (q, 2H, CH₂, J = 7.24 Hz); 6.98-7.92 (m, 8H, Ar).

^1H -NMR (CDCl_3 , δ , ppm): 1.01 (s, 3H, Si-CH₃); 1.10 (s, 3H, Si-CH₃); 1.36 (s, 9H, *t*-Bu); 1.54 (t, 3H, CH₃, J = 7.24 Hz); 4.38 (q, 2H, CH₂, J = 7.24 Hz), 7.21-8.05 (m, 8H, Ar).

CLAIMS

1. A process for preparing dihalide or monohalide metallocene compounds of formula(I)

$$(Cp)(ZR^1_m)_n(A)_rML_qL's \quad (I)$$

wherein $(ZR^1_m)_n$ is a divalent group bridging Cp and A; Z being C, Si, Ge, N or P, and the R^1 groups, equal to or different from each other, being hydrogen or linear or branched, saturated or unsaturated C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} alkylaryl or C_7-C_{20} arylalkyl groups optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements or two R^1 can form a aliphatic or aromatic C_4-C_7 ring that can bear substituents;

Cp is a substituted or unsubstituted cyclopentadienyl group, optionally condensed to one or more substituted or unsubstituted, saturated, unsaturated or aromatic rings, containing from 4 to 6 carbon atoms, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

A is O, S, NR^2 , PR^2 wherein R^2 is hydrogen, a linear or branched, saturated or unsaturated C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} alkylaryl or C_7-C_{20} arylalkyl, or A has the same meaning of Cp;

M is selected from zirconium, titanium or hafnium;

L, equal to or different from each other are selected from the group consisting of chlorine, bromine, iodine;

L' is selected from the group consisting of hydrogen a linear or branched, saturated or unsaturated C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} alkylaryl or C_7-C_{20} arylalkyl group, optionally containing one or more Si or Ge atoms;

m is 1 or 2, more specifically it is 1 when Z is N or P, and it is 2 when Z is C, Si or Ge;

n is 0, 1, 2, 3 or 4, being 0 when r is 0 or 2;

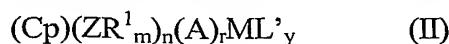
r is 0, 1 or 2;

q is 1, 2, or 3;

s is 0 or 1;

s and q satisfying the following equation: $q+s=3-r$;

said process comprising contacting a compound of formula (II)



wherein

Cp, Z, R^1 , A, M, L' , m, r and n have been described above and y is equal to $s+q$ wherein

s and q have been described above;

with an halogenating agent selected from the group consisting of $T^1L_w^1$, $T^2L_w^2$, $O=T^3L_w^3$, $R^6C(O)L$, L_2 and HL , mercury dichloride ($HgCl_2$) being excluded, wherein:

T^1 is a metal of groups 3-13 of the periodic table (new IUPAC version) or of the lanthanides series;

T^2 is a nonmetal element of groups 13-16 of the periodic table (new IUPAC version) with the exclusion of carbon;

T^3 is selected from the group consisting of C, P and S;

O is an oxygen atom bonded to T^3 through a double bond;

R^6 is selected from a linear or branched, saturated or unsaturated C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} alkylaryl or C_7-C_{20} arylalkyl;

L has the same meaning as above;

H is hydrogen;

w^1 is equal to the oxidation state of the metal T^1 ;

w^2 is equal to the oxidation state of the element T^2 ;

w^3 is equal to the oxidation state of the element T^3 minus 2.

2. The process according to claim 1 wherein divalent bridge $(ZR^1_m)_n$ is selected from the group consisting of CR^1_2 , $(CR^1_2)_2$, $(CR^1_2)_3$, SiR^1_2 , GeR^1_2 , NR^1 and PR^1 , wherein R¹ has been described in claim 1;

the ligand Cp, which is π -bonded to said metal M, is selected from the group consisting of cyclopentadienyl, mono-, di-, tri- and tetra-methyl cyclopentadienyl; 4-tertbutyl-cyclopentadienyl; 4-adamantyl-cyclopentadienyl; indenyl; mono-, di-, tri- and tetra-methyl indenyl; 4,5,6,7-tetrahydroindenyl; fluorenyl; 5,10-dihydroindeno[1,2-b]indol-10-yl; N-methyl- or N-phenyl-5,10-dihydroindeno[1,2-b]indol-10-yl; 5,6-dihydroindeno[2,1-b]indol-6-yl; N-methyl- or N-phenyl-5,6-dihydroindeno[2,1-b]indol-6-yl; azapentalene-4-yl; thiapentalene-4-yl; azapentalene-6-yl; thiapentalene-6-yl; mono-, di- and tri-methyl-azapentalene-4-yl and 2,5-dimethyl-cyclopenta[1,2-b:4,3-b']-dithiophene;

The group A has the same meaning of Cp, or it is N-methyl, N-ethyl, N-isopropyl, N-butyl, N-phenyl, N-benzyl, N-cyclohexyl and N-cyclododecyl.

3. The process according to claim 2 wherein the divalent bridge $(ZR^1_m)_n$ is selected from the group consisting of $Si(CH_3)_2$, $SiPh_2$, CH_2 , $(CH_2)_2$, $(CH_2)_3$ or $C(CH_3)_2$.
4. The process according to anyone of claims 1-3 wherein the halogenating agent is

selected from the group consisting of FeCl_3 , CuCl_2 , ZnCl_2 , BCl_3 , BBr_3 , SiCl_4 , PCl_5 , SOCl_2 , POCl_3 , $\text{CH}_3\text{C}(\text{O})\text{Cl}$, $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{O})\text{Cl}$, $\text{C}_6\text{H}_5\text{C}(\text{O})\text{Cl}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{Cl}$, Br_2 , Cl_2 , I_2 , HCl , HBr and HI .

5. A process for preparing dihalide or monohalide metallocene compounds of formula(I)

$$(\text{Cp})(\text{ZR}^1)^m(\text{A})_r\text{ML}_q\text{L}'^s \quad (\text{I})$$

wherein M, Cp, A, Z, R¹, r, m, n, q, s, L and L' have the meaning reported in anyone of claims 1-4 comprising the following steps:

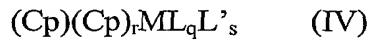
 - a) reacting a ligand of formula $(\text{Y-Cp})(\text{ZR}^1)^m(\text{A-Y})_r$ or when n is 0 a mixture of ligands Y-Cp and r(A-Y) with an amount EQ of a compound of formula L'_jB or L'MgL'' such that $\text{EQ} \geq 1+r$ molar equivalents with respect to Cp, wherein Cp, A, Z, R¹, m, r, q, and L' have the meaning reported above; L'' is selected from the group consisting of chlorine, bromine, iodine; n is an integer having values 1, 2, 3 or 4; the groups Y, the same or different from each other, are suitable leaving groups; Mg is magnesium; B is an alkaline or alkaline-earth metal; and j is 1 or 2, j being equal to 1 when B is an alkali metal, and j being equal to 2 when B is an alkaline-earth metal;
 - b) reacting the product obtained from step a) with at least 1 molar equivalent of a compound of formula ML''₄, wherein M have the meaning reported above, L'' is selected from the group consisting of chlorine, bromine, iodine;
 - c) if the amount EQ of a compound of formula L'_jB or L'MgL'' added in step a) is less than $1+r+q$, adding to the reaction mixture an amount of a compound of formula L'_jB or L'MgL'' equal to or higher than $1+r+q-EQ$ molar equivalents;
 - d) optionally purifying the mixture and separating the racemic and the meso forms; and
 - e) reacting the mixture with an halogenating agent selected from the group consisting of: T^1L_w^1 ; T^2L_w^2 ; $\text{O}=\text{T}^3\text{L}_w^3$; $\text{R}^6\text{C}(\text{O})\text{L}$; L_2 and HL wherein T^1 , T^2 , T^3 , L , w^1 , w^2 , w^3 and R^6 have been described in anyone of claims 1-4.
6. The process according to claim 5 wherein the amount EQ added in step a) is such that $1+r \leq \text{EQ} \geq 1+r+q$;
7. The process according to claim 5 wherein the amount EQ added in step a) is such that $\text{EQ} = 1+r+q$;
8. The process according to anyone of claims 5-7 for preparing dihalide or monohalide metallocene compounds of formula (III):



wherein M, Cp, A, Z, R¹, m, q, s, L and L' have the meaning reported in anyone of claims 1-7 and n is an integer having values 1, 2, 3 or 4; comprising the following steps:

- a) reacting a ligand of formula (Y-Cp)(ZR¹_m)_n(A-Y) with at least 2+q molar equivalents with respect to Cp of a compound of formula L'_jB or L''MgL'', wherein Cp, A, Z, R¹, L' and m have been described above, L'' is selected from the group consisting of chlorine, bromine, iodine; n is an integer having values 1, 2, 3 or 4; the groups Y, the same or different from each other, are suitable leaving groups; Mg is magnesium; B is an alkaline or alkaline-earth metal; and j is 1 or 2, j being equal to 1 when B is an alkali metal, and j being equal to 2 when B is an alkaline-earth metal;
- b) reacting the product obtained from step a) with at least 1 molar equivalent of a compound of formula ML''₄, wherein M have the meaning reported above, L'' is selected from the group consisting of chlorine, bromine, iodine;
- c) optionally purifying the mixture and separating the racemic and the meso forms; and
- d) reacting the mixture with an halogenating agent selected from the group consisting of: T¹L_w¹; T²L_w²; O=T³L_w³; R⁶C(O)L; L₂ and HL wherein T¹, T², T³, L, w¹, w², w³ and R⁶ have been described in anyone of claims 1-7.

9. The process according to anyone of claims 5-7 for preparing dihalide or monohalide metallocene compounds of formula (IV):



wherein M, Cp, M, L, L', r, q and s have been described in any of claims 1-7 comprising the following steps:

- a) reacting 1+r equivalent of a ligand of formula (Y-Cp) with at least 3+r molar equivalents of a compound of formula L_jB or L''''MgL', wherein Cp, L'''' and L' have the meaning reported in anyone of claims 1-5; the groups Y, the same or different from each other, are suitable leaving groups; B is an alkaline or alkaline-earth metal; and j is 1 or 2, j being equal to 1 when B is an alkali metal, and j being equal to 2 when B is an alkaline-earth metal;
- b) reacting the product obtained from step a) with at least 1 molar equivalent of a compound of formula ML''₄, wherein M have the meaning reported above, L'' is selected from the group consisting of chlorine, bromine;
- c) optionally purifying the mixture; and

- d) reacting the mixture with an halogenating agent selected from the group consisting of: $T^1L_w^1$; $T^2L_w^2$; $O=T^3L_w^3$; $R^6C(O)L$; L_2 and HL wherein T^1 , T^2 , T^3 , L , w^1 , w^2 , w^3 , R^6 have been described in anyone of claims 1-4.
- 10. The process according to anyone of claims 1-9 wherein the reactions are carried out in an aprotic polar or apolar solvent.
- 11. The process according to anyone of claims 5-10 wherein the leaving group Y is hydrogen.
- 12. The process according to anyone of claims 5-11 wherein L' is selected from the group consisting of methyl, ethyl, n-butyl, sec-butyl, phenyl, benzyl and $-CH_2Si(CH_3)_3$; the substituents and L'' is bromine or iodine.
- 13. The process according to anyone of claims 5-11 wherein the reactant ML''_4 is selected from the group consisting of $TiCl_4$, $ZrCl_4$, $HfCl_4$.

DERWENT-ACC-NO: 2003-120414**DERWENT-WEEK:** 200765*COPYRIGHT 2008 DERWENT INFORMATION LTD*

TITLE: Preparation of dihalide or monohalide metallocene compound used as catalyst in olefin polymerization, involves contacting metallocene compound of specific formula with halogenating agent

INVENTOR: BALBONI D; RESCONI L

PATENT-ASSIGNEE: BASELL POLYOLEFINE GMBH [BASE] , BALBONI D [BALBI] , RESCONI L [RESCI]

PRIORITY-DATA: 2001EP-201327 (April 10, 2001)**PATENT-FAMILY:**

PUB-NO	PUB-DATE	LANGUAGE
WO 02083699 A2	October 24, 2002	EN
EP 1381618 A2	January 21, 2004	EN
US 20040147770 A1	July 29, 2004	EN
JP 2004531529 W	October 14, 2004	JA
US 6987196 B2	January 17, 2006	EN
US 20060025621 A1	February 2, 2006	EN
US 7115761 B2	October 3, 2006	EN
JP 3986441 B2	October 3, 2007	JA

DESIGNATED-STATES: JP US AT BE CH CY DE DK ES FI FR GB
GR IE IT LU MC NL PT SE TR AL AT BE
CH CY DE DK ES FI FR GB GR IE IT LI
LT LU LV MC MK NL PT RO SE SI TR

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
WO2002083699A2	N/A	2002WO-EP03697	April 3, 2002
EP 1381618A2	N/A	2002EP-745208	April 3, 2002
JP2004531529W	N/A	2002JP-581454	April 3, 2002
JP 3986441B2	N/A	2002JP-581454	April 3, 2002
EP 1381618A2	N/A	2002WO-EP03697	April 3, 2002
US20040147770A1	N/A	2002WO-EP03697	April 3, 2002
JP2004531529W	N/A	2002WO-EP03697	April 3, 2002
US 6987196B2	N/A	2002WO-EP03697	April 3, 2002
JP 3986441B2	N/A	2002WO-EP03697	April 3, 2002
US20040147770A1	N/A	2003US-474596	October 9, 2003
US 6987196B2	N/A	2003US-474596	October 9, 2003
US20060025621A1	N/A	2005US-237588	September 27, 2005
US 7115761B2	Based on	2005US-237588	September 27, 2005

INT-CL-CURRENT:

TYPE	IPC DATE
CIPP	C07F17/00 20060101
CIPP	C07F7/00 20060101
CIPS	B01J31/00 20060101

CIPS	C07F17/00 20060101
CIPS	C07F7/28 20060101
CIPS	C07F7/28 20060101
CIPS	C07F9/28 20060101
CIPS	C08F10/00 20060101
CIPS	C08F10/00 20060101
CIPS	C08F4/44 20060101
CIPS	C08F4/64 20060101
CIPS	C08F4/64 20060101
CIPS	C08F4/6592 20060101
CIPN	B01J31/00 20060101
CIPN	C08F4/44 20060101

ABSTRACTED-PUB-NO: WO 02083699 A2

BASIC-ABSTRACT:

NOVELTY - A metallocene compound (II) is contacted with a halogenating agent, to produce a dihalide or monohalide metallocene compound (I).

DESCRIPTION - A metallocene compound of formula (II) is contacted with a halogenating agent chosen from T1Lw1, T2Lw2, O=T3Lw3, R6C(O)L, L2 and HL, where mercury dichloride (HgCl₂) is excluded, to produce a dihalide or monohalide metallocene compound of formula (I).

(Cp)(ZR_{1m})_n(A)rMLqL's (I)

(Cp)(ZR_{1m})_n(A)rML'y (II)

(ZR_{1m})_n = divalent group bridging Cp and A;

Z = carbon, silicon, germanium, nitrogen or phosphorus;

R₁ = H, linear or branched, (un)saturated 1-20C alkyl, 3-20C cycloalkyl, 6-20C aryl, 7-20C alkylaryl or 7-20C

arylalkyl optionally containing one or more heteroatoms belonging to groups 13-17, or two R1 can form an aliphatic or aromatic 4-7C ring which can bear substituent;

Cp = (un)substituted cyclopentadienyl group, optionally condensed to one or more (un)substituted, (un)saturated or aromatic rings, containing 4-6C, optionally containing one or more heteroatoms belonging to groups 13-17;

A = Cp, oxygen, sulfur, NR2, PR2;

R2 = H, linear or branched, (un)saturated 1-20C alkyl, 3-20C cycloalkyl, 6-20C aryl, 7-20C alkylaryl or 7-20C arylalkyl;

M = zirconium, titanium or hafnium;

L = chlorine, bromine or iodine;

L' = H, or linear or branched, (un)saturated 1-20C alkyl, 3-20C cycloalkyl, 6-20C aryl, 7-20C alkylaryl or 7-20C arylalkyl, optionally containing one or more silicon or germanium atoms;

m = 1 or 2, preferably 1 when Z is nitrogen or phosphorus, and 2 when Z is carbon, silicon or germanium;

n = 0-4, being 0 when r is 0 or 2;

r = 0-2;

q = 1-3;

s = 0 or 1;

s and q = satisfy the equation given by q+s = 3-r;

y = s+q;

T1 = metal of groups 3-13 or of lanthanide series;

T2 = non-metal element of groups 13-16 with the exclusion of carbon;

T3 = carbon, phosphorus or sulfur;

O = oxygen atom bonded to T3 through a double bond;

R6 = linear or branched, (un)saturated 1-20C alkyl, 3-20C cycloalkyl, 6-20C aryl, 7-20C alkylaryl or 7-20C arylalkyl;

H = hydrogen;

w1 = oxidation state of T1;

w2 = oxidation state of T2; and

w3 = oxidation state of T3 minus 2.

USE - For preparing dihalide or monohalide metallocene compounds used as catalysts for olefin polymerization.

ADVANTAGE - The preparation process provides monohalide or dihalide metallocene compounds having high purity and yield. The product is purified easily due to the better solubility of the formed intermediate alkylated metallocene with respect to the dihalide or monohalide product. The racemic and meso forms are also easily separated.

EQUIVALENT-ABSTRACTS:

ORGANIC CHEMISTRY

Preferred Process: The dihalide or monohalide metallocene compound (I) is prepared by reacting a ligand of formula (A) or, when n is 0, a mixture of ligands of formula (B) and (C), with an amount EQ of a compound of formula (D) or (E) such that EQ at least 1+r molar equivalents with respect to Cp. The product obtained is reacted with at least 1 molar equivalent of a compound of formula (F) . If

the amount EQ of a compound of formula (D) or (E) is less than 1+r+q, then an amount of (D) or (E) equal to or higher than 1+r+q-EQ molar equivalents is added to the reaction mixture. The mixture is optionally purified and the racemic and meso forms are separated. The mixture with the halogenating agent is chosen from T1Lw1, T2Lw2, O=T3Lw3, R6C(O)L, L2 and HL.

(Y-Cp) (ZR1m)_n (A-Y)_r (A)

Y-Cp (B)

r (A-Y) (C)

L'jB (D)

L'MgL' (E)

ML4 (F)

M, Cp, A, Z, R1, r, m, n, q, s, L, L', T1, T2, T3, w1, w2, w3 and R6 = as defined above;

L and L' = chlorine, bromine or iodine;

y = leaving groups;

Mg = magnesium;

B = alkaline or alkaline earth metal; and

j = 1 or 2, being 1 when B is an alkali metal and being 2 when B is an alkaline earth metal.

Preferred Compounds: The preferred metallocene compounds of formula (I) are compounds of formula (III) or compounds of formula (IV).

(Cp) (ZR1m)_n (A) MLqL's (III)

(Cp) (Cp) rMLqL's (IV)

n = value other than 0; and

r = 1.

Preferred Definitions:

(ZR1m)_n = CR12, (CR12)₂, (CR12)₃, SiR12, GeR12, NR1 or PR1, preferably Si(CH₃)₂, SiPh₂, CH₂, (CH₂)₂, (CH₂)₃ or C(CH₃)₂;

Cp = pi-bonded to M, and is chosen from cyclopentadienyl, mono-, di-, tri- and tetra-methyl cyclopentadienyl, 4-tert-butyl-cyclopentadienyl, 4-adamantyl-cyclopentadienyl, indenyl, mono-, di-, tri- and tetra-methyl indenyl, 4,5,6,7-tetrahydroindenyl, fluorenyl, 5,10-dihydroindeno(1,2-b)indol-10-yl, N-methyl- or N-phenyl-5,10-dihydroindeno(1,2-b)indol-10-yl, 5,6-dihydroindeno(2,1-b)indol-6-yl, N-methyl- or N-phenyl-5,6-dihydroindeno(2,1-b)indol-6-yl, azapentalene-4-yl, thiapentalene-4-yl, azapentalene-6-yl, thiapentalene-6-yl, mono-, di- and tri-methyl-azapentalene-4-yl and 2,5-dimethyl-cyclopenta(1,2-b:4,3-b')-dithiophene;

A = Cp, or N-methyl, N-ethyl, N-isopropyl, N-butyl, N-phenyl, N-benzyl, N-cyclohexyl and N-cyclododecyl; and

L = methyl, ethyl, n-butyl, sec-butyl, phenyl, benzyl or -CH₂Si(CH₃)₃.

SPECIFIC COMPOUNDS

The halogenating agent is chosen from 19 claimed compounds such as ferric chloride, copper chloride and zinc chloride.

Several metallocene compounds are disclosed, such as bis(indenyl)zirconium dichloride and bis(fluorenyl)zirconium dichloride.

A solution of methyl lithium (MeLi) (15.8 ml) in diethylether (Et₂O) was added at room temperature to a

solution of indene (1.5 g) in Et₂O (30 ml) over a period of about 5 minutes. The mixture was stirred for 30 minutes, to give an orange solution. Zirconium chloride (ZrCl₄) (1.47 g) was slurried in pentane (30 ml). The ZrCl₄ slurry in pentane was quickly added to the lithium salt solution in Et₂O. The reaction mixture was stirred for 30 minutes, and the yellow-brown suspension was treated, to give a light yellow solid (1.92 g) (86.5% yield) which was characterized as pure Ind₂ZrMe₂.

TITLE-TERMS: PREPARATION METALLOCENE COMPOUND CATALYST OLEFIN POLYMERISE CONTACT SPECIFIC FORMULA HALOGENATED AGENT

DERWENT-CLASS: A17 E11 E12

CPI-CODES: A02-A06E1; A04-G01A; E05-E01; E05-E02C; E05-E02D; E05-F02; E05-G; E05-L; E05-L01; E05-M; E05-N; E11-F08;

CHEMICAL-CODES: Chemical Indexing M3 *01* Fragmentation Code A422 A910 B514 B720 B731 B743 B831 C017 C100 C720 C801 C803 C804 C805 C806 C807 G037 G551 M210 M211 M214 M233 M240 M250 M273 M281 M283 M320 M411 M510 M520 M530 M540 M541 M640 M720 N104 N209 N225 N513 N514 N515 Q121 Specific Compounds RA9200 Registry Numbers 639402

Chemical Indexing M3 *02* Fragmentation Code A540 A923 A940 C017 C100 C720 C801 C803 C804 C805 C806 C807 G031 G032 G039 G211 G299 M1 M124 M125 M126 M144 M280 M320 M411 M510 M520 M531 M532 M540 M640 M720 N104 N209 N225 N513 N514 N515 Q121 Specific Compounds RA0M9Y Registry Numbers 229663

Chemical Indexing M3 *03* Fragmentation Code A540 A923 A940 C053 C100 C720 C801 C803 C804 C805 C806 C807 G031 G032 G039 G211 G299 M1 M124 M125 M126 M144 M280

M320 M411 M510 M520 M532 M540 M640 M720
N104 N209 N225 N513 N514 N515 Q121
Specific Compounds RA92XQ Registry
Numbers 639753

Chemical Indexing M3 *04* Fragmentation
Code A540 A910 A923 A940 C017 C100 C720
C801 C803 C804 C805 C806 C807 G031 G032
G039 G211 G299 M1 M124 M125 M126 M144
M210 M211 M250 M281 M320 M411 M510 M520
M530 M532 M540 M640 M720 N104 N209 N225
N513 N514 N515 Q121 Specific Compounds
RA92XT Registry Numbers 639756

Chemical Indexing M3 *05* Fragmentation
Code A332 A422 A540 A672 A910 A922 A923
A940 A960 B514 B605 B614 B615 B633 B720
B730 B731 B742 B743 B744 B760 B803 B813
B823 B831 B840 C000 C017 C035 C100 C101
C316 C550 C720 C801 C803 C804 C805 C806
C807 D000 D010 D011 D013 D014 D015 D016
D019 D020 D021 D022 D023 D024 D029 D030
D220 D320 D399 D420 D690 D699 E160 E310
E350 G010 G019 G020 G021 G029 G030 G031
G032 G033 G034 G036 G037 G038 G039 G040
G100 G111 G112 G113 G211 G299 G310 G399
G400 G460 G480 G551 G599 G640 G699 G710
G810 G820 H102 H103 H141 H181 H201 H202
H401 H441 H481 H713 H715 H716 H721 H722
K441 M113 M115 M119 M121 M122 M123 M124
M125 M126 M129 M144 M150 M210 M211 M212
M213 M214 M215 M216 M220 M221 M222 M223
M224 M225 M226 M231 M232 M233 M240 M250
M272 M273 M280 M281 M282 M283 M320 M411
M417 M510 M511 M520 M530 M531 M532 M533
M540 M541 M542 M630 M640 M650 M720 N104
N209 N225 N513 N514 N515 Q121 Markush
Compounds 008181901

Chemical Indexing M3 *06* Fragmentation
Code A923 A940 A960 B514 B605 B614 B615
B633 B720 B730 B731 B742 B743 B744 B760

B803 B813 B823 B831 B840 C000 C017 C035
C100 C101 C316 C550 C720 C801 C803 C804
C805 C806 C807 D000 D010 D011 D013 D014
D015 D016 D019 D020 D021 D022 D023 D024
D029 D030 D220 D320 D399 D420 D690 D699
E160 E310 E350 G010 G019 G020 G021 G029
G030 G031 G032 G033 G034 G036 G037 G038
G039 G040 G100 G111 G112 G113 G211 G299
G310 G399 G400 G460 G480 G551 G599 G640
G699 G710 G810 G820 H102 H103 H141 H181
H201 H202 H401 H441 H481 H713 H715 H716
H721 H722 K441 M113 M115 M119 M121 M122
M123 M124 M125 M126 M129 M144 M150 M210
M211 M212 M213 M214 M215 M216 M220 M221
M222 M223 M224 M225 M226 M231 M232 M233
M240 M250 M272 M273 M280 M281 M282 M283
M320 M411 M417 M510 M511 M520 M530 M531
M532 M533 M540 M541 M542 M630 M640 M650
M720 N104 N209 N225 N513 N514 N515 Q121
Markush Compounds 008181902

Chemical Indexing M3 *07* Fragmentation
Code A923 A940 A960 B514 B605 B614 B615
B633 B720 B730 B731 B742 B743 B744 B760
B803 B813 B823 B831 B840 C000 C017 C035
C100 C101 C316 C550 C720 C801 C803 C804
C805 C806 C807 D000 D010 D011 D013 D014
D015 D016 D019 D020 D021 D022 D023 D024
D029 D030 D220 D320 D399 D420 D690 D699
E160 E310 E350 G010 G019 G020 G021 G029
G030 G031 G032 G033 G034 G036 G037 G038
G039 G040 G100 G111 G112 G113 G211 G299
G310 G399 G400 G460 G480 G551 G599 G640
G699 G710 G810 G820 H102 H103 H141 H181
H201 H202 H401 H441 H481 H713 H715 H716
H721 H722 K441 M113 M115 M119 M121 M122
M123 M124 M125 M126 M129 M144 M150 M210
M211 M212 M213 M214 M215 M216 M220 M221
M222 M223 M224 M225 M226 M231 M232 M233
M240 M250 M272 M273 M280 M281 M282 M283
M320 M411 M417 M510 M511 M520 M530 M531
M532 M533 M540 M541 M542 M630 M640 M650

M720 N104 N209 N225 N513 N514 N515 Q121
Markush Compounds 008181903

Chemical Indexing M3 *08* Fragmentation
Code A923 A940 A960 B514 B605 B614 B615
B633 B720 B730 B731 B742 B743 B744 B760
B803 B813 B823 B831 B840 C000 C017 C035
C100 C101 C316 C550 C720 C801 C803 C804
C805 C806 C807 D000 D010 D011 D013 D014
D015 D016 D019 D020 D021 D022 D023 D024
D029 D030 D220 D320 D399 D420 D690 D699
E160 E310 E350 G010 G019 G020 G021 G029
G030 G031 G032 G033 G034 G036 G037 G038
G039 G040 G100 G111 G112 G113 G211 G299
G310 G399 G400 G460 G480 G551 G599 G640
G699 G710 G810 G820 H102 H103 H141 H181
H201 H202 H401 H441 H481 H713 H715 H716
H721 H722 K441 M113 M115 M119 M121 M122
M123 M124 M125 M126 M129 M144 M150 M210
M211 M212 M213 M214 M215 M216 M220 M221
M222 M223 M224 M225 M226 M231 M232 M233
M240 M250 M272 M273 M280 M281 M282 M283
M320 M411 M417 M510 M511 M520 M530 M531
M532 M533 M540 M541 M542 M630 M640 M650
M720 N104 N209 N225 N513 N514 N515 Q121
Markush Compounds 008181904

Chemical Indexing M3 *09* Fragmentation
Code A923 A940 A960 B514 B605 B614 B615
B633 B720 B730 B731 B742 B743 B744 B760
B803 B813 B823 B831 B840 C000 C017 C035
C100 C101 C316 C550 C720 C801 C803 C804
C805 C806 C807 D000 D010 D011 D013 D014
D015 D016 D019 D020 D021 D022 D023 D024
D029 D030 D220 D320 D399 D420 D690 D699
E160 E310 E350 G010 G019 G020 G021 G029
G030 G031 G032 G033 G034 G036 G037 G038
G039 G040 G100 G111 G112 G113 G211 G299
G310 G399 G400 G460 G480 G551 G599 G640
G699 G710 G810 G820 H102 H103 H141 H181
H201 H202 H401 H441 H481 H713 H715 H716
H721 H722 K441 M113 M115 M119 M121 M122

M123 M124 M125 M126 M129 M144 M150 M210
M211 M212 M213 M214 M215 M216 M220 M221
M222 M223 M224 M225 M226 M231 M232 M233
M240 M250 M272 M273 M280 M281 M282 M283
M320 M411 M417 M510 M511 M520 M530 M531
M532 M533 M540 M541 M542 M630 M640 M650
M720 N104 N209 N225 N513 N514 N515 Q121
Markush Compounds 008181905

Chemical Indexing M3 *10* Fragmentation
Code A923 A940 A960 B514 B605 B614 B615
B633 B720 B730 B731 B742 B743 B744 B760
B803 B813 B823 B831 B840 C000 C017 C035
C100 C101 C316 C550 C720 C801 C803 C804
C805 C806 C807 D000 D010 D011 D013 D014
D015 D016 D019 D020 D021 D022 D023 D024
D029 D030 D220 D320 D399 D420 D690 D699
E160 E310 E350 G010 G019 G020 G021 G029
G030 G031 G032 G033 G034 G036 G037 G038
G039 G040 G100 G111 G112 G113 G211 G299
G310 G399 G400 G460 G480 G551 G599 G640
G699 G710 G810 G820 H102 H103 H141 H181
H201 H202 H401 H441 H481 H713 H715 H716
H721 H722 K441 M113 M115 M119 M121 M122
M123 M124 M125 M126 M129 M144 M150 M210
M211 M212 M213 M214 M215 M216 M220 M221
M222 M223 M224 M225 M226 M231 M232 M233
M240 M250 M272 M273 M280 M281 M282 M283
M320 M411 M417 M510 M511 M520 M530 M531
M532 M533 M540 M541 M542 M630 M640 M650
M720 N104 N209 N225 N513 N514 N515 Q121
Markush Compounds 008181906

Chemical Indexing M3 *11* Fragmentation
Code A422 A910 A923 A940 C017 C100 C720
C801 C803 C804 C805 C806 C807 D011 D021
D022 D023 D029 E310 H1 H102 H161 H181 H2
H201 M210 M212 M214 M233 M273 M282 M320
M411 M511 M520 M530 M540 M640 M720 N104
N209 N225 N513 N514 N515 Q121 Ring Index
Numbers 04248 Markush Compounds
008181907

ENHANCED-POLYMER-INDEXING: Polymer Index [1.1] 018 ;
G0033*R G0022 D01 D02 D51
D53; H0000; H0011*R; L9999
L2573 L2506; L9999 L2528
L2506; P1150;

Polymer Index [1.2] 018 ;
ND02;

Polymer Index [1.3] 018 ; D01
D05 D07 D08 D11 D10 D12 D13*R
D14 D13 D15 D16 D17 D18*R D19
D18 D21 D25 D22 D31 D32 D33
D34 D35 D73 D74 D75 D76 D77
D78 D79 D41 D47 D53 D51 D54
D55 D56 D57 D59 D62 D61 D68
D69 D70 D71 D85 D86 D87 D88
D89 D90 D91 D92 D93 D94 D95
F00 F04 F08 F07 F09 F10 F11
F50 F83 F86 F87 Ti 4B Tr Zr
Hf Cl 7A Br I* Ge 4A O* 6A P*
5A N* 3A*R 4A*R 5A*R 6A*R
7A*R; C999 C033 C000; C999
C248; C999 C293;

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: 2003-031004